



PATENT
KEL01 P-126

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Murray Orpin
Serial No. : 10/715,948
Filed : November 18, 2003
For : A SYNTACTIC PHENOLIC FOAM COMPOSITION
Confirmation No. : 4448
Group : 1711

Commissioner for Patents
P.O. Box 1450
Alexandria VA 22313-1450

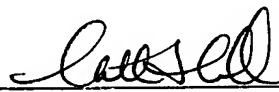
Dear Sir:

CERTIFICATE OF MAIL

I certify that the attached return postcard, Claim of Priority, and a certified copy of the United Kingdom patent application are being deposited with the United States Postal Service as first class mail in an envelope addressed to:

Commissioner for Patents
P.O. Box 1450
Alexandria VA 22313-1450

on February 25, 2004.


Catherine S. Collins
Van Dyke, Gardner, Linn & Burkhart, LLP
P.O. Box 888695
Grand Rapids, MI 49588-8695
(616) 975-5500

CSC:lmisc
Enclosures



W. H. H. H.

W. H. H. H.



PATENT
KEL01 P-126

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Murray Orpin
For : A SYNTACTIC PHENOLIC FOAM COMPOSITION
Serial No. : 10/715,948
Filing Date : November 18, 2003
Confirmation No. : 4448

Commissioner for Patents
P.O. Box 1450
Alexandria VA 22313-1450

Dear Sir:

CLAIM OF PRIORITY

Applicant hereby claims the priority benefits under the provisions of 35 U.S.C. 119, basing said claim of priority on United Kingdom patent application Serial No. 0226773.0, filed November 18, 2002.

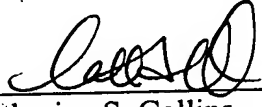
In accordance with the provisions of 35 U.S.C. 119 and 37 C.F.R. 1.55(a), certified copies of the above listed United Kingdom patent application is attached.

Respectfully submitted,

MURRAY ORPIN

By: Van Dyke, Gardner, Linn & Burkhart, LLP

Dated: February 25, 2004.


Catherine S. Collins
Registration No. 37 599
Suite 207
2851 Charlevoix Drive, S.E.
P.O. Box 888695
Grand Rapids, Michigan 49588-8695
(616) 975-5500

CSC:lmsc



1. The first part of the document is a letter from the Director of the Central Intelligence Agency to the President of the United States, dated January 19, 1960. The letter is titled "The Situation in the Middle East" and discusses the current state of affairs in the region, including the recent developments in the Arab-Israeli conflict and the role of the United States in the area.

2. The second part of the document is a report from the Central Intelligence Agency, dated January 19, 1960, titled "The Situation in the Middle East". This report provides a detailed analysis of the current state of affairs in the region, including the recent developments in the Arab-Israeli conflict and the role of the United States in the area.



INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed *Andrew Jones*

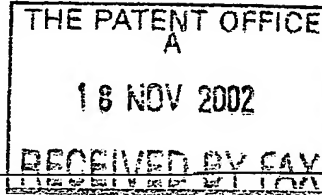
Dated 14 November 2003

Patents Form 1/77

Patents Act 1977
(Rule 16)The
Patent
Office18NOV02 E764110-1 C61838
P01/7700 0.00-0226773.0

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road
Newport
South Wales
NP9 1RH

1. Your reference

Fb05750/MOC/pd

2. Patent application number

(The Patent Office will fill in this part)

0226773.0

18 NOV 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

PYRO TECHNOLOGIES LIMITED
Hillcourt Farm, Frogmarsh
Eldersfield
Gloucestershire GL19 4PW
United Kingdom

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

8508582001

4. Title of the invention "A Syntactic Phenolic Foam Composition"

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom
to which all correspondence should be sent
(including the postcode)~~University Street~~
~~Belfast~~
~~BT7 1FY~~
~~Northern Ireland~~
~~United Kingdom~~MAURA O'CONNELL,
4 MOUNT CHARLES,
BELFAST,
BT7 1WZ
NORTHERN IRELAND
UNITED KINGDOM
7774417001
08752156001

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)Date of filing
(day / month / year)

NA

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

NA

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Patents Form 1/77

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	0
Description	17
Claim(s)	0
Abstract	0
Drawing(s)	0

10. If you are also filing any of the following, state how many against each item.

Priority documents	0
Translations of priority documents	0
Statement of inventorship and right to grant of a patent (<i>Patents Form 7/77</i>)	0
Request for preliminary examination and search (<i>Patents Form 9/77</i>)	0
Request for substantive examination (<i>Patents Form 10/77</i>)	0
Any other documents (please specify)	0

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

12/10/2002

PYRO TECHNOLOGIES LIMITED

12. Name and daytime telephone number of person to contact in the United Kingdom

Maura O'Connell - 028 9023 6000

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered "Yes" Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

Patents Form 1/77

"A Syntactic Phenolic Foam Composition"

The present invention relates to a syntactic phenolic foam composition.

5 Essentially, the present invention hinges on the potential to form tough, lightweight, fire resisting materials from the synergistic combination of a specific, highly reactive, phenolic resin and specific thermoplastic microspheres. Although this has been vaguely mentioned in early patent literature, there have been no recent developments at all. Thus, the literature is completely silent on the specific
10 properties (defined limits) necessary to achieve the objects of the present invention. More particularly, the specific phenolic resin type is crucial to all aspects of the present invention, not least because water occurs as a system diluent in all cases and this resin is uniquely able to produce the described materials rapidly without being dramatically slowed or weakened by the presence of such
15 water.

Prior Art

20 The general concept of a syntactic phenolic foam composition comprising a combination of thermoplastic microspheres (whether expandable or expanded) together with a phenolic resin has been generically disclosed. Specifically, US-A-4,067,829 discloses certain cured resole resins, having a reduced tendency to corrode steel. These resole resins may optionally contain expandable
microspheres as a foaming agent.

25

Objects of the Invention

It is an object of the invention to provide a range of structural syntactic foam compositions with improved fire resistance compatible with the requirements of
30 the aerospace, construction, offshore and transportation industries.

By "structural" is meant the ability to bear either static or cyclic loads consistent with the intended final application of the manufactured component, where such application is defined as structural or semi-structural in nature. Conventional phenolic foams are not suitable for such applications due to their brittle, friable nature.

It is a further object of the invention to

1. Produce a range of materials that are highly cost efficient within their intended field of application;
2. Define flexible and facile processing that is capable of producing finished components rapidly with minimal secondary operations;
3. Offer a phenolic resin based foam that is effectively pH neutral in service and is therefore free of corrosion risk;
4. Define a wide range of foam densities that may be produced from the materials technology; and/or
5. Provide example of specific engineered materials systems with optimised performance in their intended fields.

Statements of Invention

According to the present invention there is provided a syntactic phenolic foam composition comprising a highly reactive phenolic resole resin having a viscosity between 2,000-5,000cP at 25°C, and a water content of 2-5% (w/w) and, preferably, a free phenol content of 12-15% (w/w); a catalyst for curing the phenolic resole resin; and thermally expandable and / or expanded thermoplastic microspheres, the microspheres comprising a thermoplastic polymer shell made of a copolymer of 93 to 40 parts by weight of a nitrile-containing, ethylenically unsaturated monomer and 7 to 60 parts by weight of another ethylenically unsaturated monomer, and a propellant trapped within the polymer shell.

Preferably, the phenolic resole resin has a viscosity of between 3,000-4,000cP at 25°C and/or a water content of 3-4% (w/w). The said resin is capable of fully crosslinking at ambient temperatures of >15°C and will achieve peak exotherm temperatures of 155-170°C in conjunction with mild ester-based catalysts such as

5 Hordaphos CCMS ex Clariant AG. Testing is based on 30g resin at 25°C (held in a 45mm diameter x 110mm high test tube) catalysed with 7% w/w catalyst. Peak exotherm should occur in <10 minutes without any input of external heat.

It will be appreciated that it is critical that the phenolic resole resin is highly

10 reactive but that its viscosity and water content, as defined hereinabove, are but indirect guides to the required highly reactive nature of the phenolic resole resin. For these reasons, the parameters defining this high reactivity can be amended or modified, as will be appreciated by those skilled in the art.

1.5 Thermoplastic Microspheres

The Dow Chemical Company originally developed expanding thermoplastic microspheres and the current main supplier is Akzo Nobel, under the Registered Trade Mark Expancel. Suitable microspheres for use in the present invention are

20 either expandable and / or expanded thermoplastic microspheres, or a mixture thereof and comprise a thermoplastic polymer shell made of a copolymer of 93 to 40 parts by weight of a nitrile-containing, ethylenically unsaturated monomer and 7 to 60 parts by weight of another ethylenically unsaturated monomer, entrapping

25 a propellant therewithin. The spheres expand by heating above the boiling point of the propellant and above the softening point of the polymer shell.

Suitable nitrile-containing, ethylenically unsaturated monomers include, but are not limited to, one or more of acrylonitrile, methacrylonitrile, α -chloroacrylonitrile, α -ethoxyacrylonitrile, fumaroacrylonitrile, crotoacrylonitrile,

30 of which acrylonitrile is preferred.

Suitable other ethylenically unsaturated monomers include, but are not limited to acrylic esters, methacrylic esters, vinyl chloride, vinylidene chloride, vinyl pyridine, vinyl esters, styrenes and derivatives or mixtures thereof, of which vinylidene chloride and / or vinyl chloride are preferred.

5

Of the thermoplastic microspheres currently commercially available, the Expanded grades 551DU (Dry Unexpanded) and 551WE (Wet Expanded) are preferred for the utilities of the present invention. The 551 grade has a polymer shell comprising a copolymer of monomers of vinylidene chloride (PVDC) and
10 acrylonitrile (PAN) and housing a liquid volatile propellant, isobutane. Softening of this copolymer should begin in the range 93-98°C and maximum expansion of this copolymer should occur in the range of 129-148°C (maximum expansion in the 551 grade being directly dependent on the particle size). However, in the presence of phenolic resole resin, the shells are plasticised and partially solvated
15 so that expansion may begin at around 55°C. In contrast to the microspheres suitable for use in the present invention, pure PAN microspheres and other derived copolymers will rupture and dissolve in resole resin within 24 hours at ambient temperature or much more quickly between 30-40°C.

20 The choice of the 551 grade is therefore important for the stability of a mixed system, which would require bulk storage for up to 2 months, typically. It is also known that storage of the resin/microsphere blend also brings about maturation in the system, which leads to optimum expansion in the process. The unexpanded grade is less sensitive to storage maturation than the expanded grade, which has
25 much thinner cell wall. In the latter event, long term storage is not feasible unless the resin forms less than 35% of the mixed mass (i.e., 2:1 (w/w) 551WE to resin). This is relevant to the embodiment exemplified in Example 3 where it becomes necessary to produce a daily blend or possibly combine the wet expanded microspheres with the catalyst in the appropriate ratio to produce a syntactic
30 catalyst that is sufficiently stable.

The propellant is a volatile liquid trapped within the polymer shell. Suitable propellants include various short chain alkanes and short chain isoalkanes such as isopentane, isobutane, n-butane and pentane or mixtures thereof.

5 Phenolic Resin

The phenolic resin, which must be highly reactive, is used to bind the contacting points of fine-hollow thermoplastic microparticles, as well as any other beneficial functional additives present.

10

The phenolic resole resin must be a 'pure' phenolic resole produced from phenol with a molar excess of formaldehyde in the presence of sodium hydroxide as a condensation catalyst. Normally, the process temperature in production would be carefully increased to around 60°C and held there for a period of ca. 1 hour, after
15 which the temperature would be increased to around 80°C for a period of 2-4 hours. The exact times are dependent on batch size. However the two stages essentially are:

- 20 (1) Ring Substitution @ 60°C by formaldehyde into the phenol aromatic ring
(2) Condensation Polymerisation @ 80°C to increase Mol Wt

The present resin is obtainable, for example, by only heating to 60°C for a period of 5 hours on the above scale (equivalent to ca. 3.5 hours on a laboratory scale).

This leads to maximum substitution by methylol ($-\text{CH}_2\text{OH}$) groups and only low
25 molecular weight build. Most of the process and reaction water is then distilled off down to a level of around 3% resulting in a highly reactive prepolymer. It is believed that the level of reactivity obtainable by this process is highly desirable for success in this invention.

30 The phenolic resoles disclosed in the prior art are, by contrast, reacted at temperatures between 65-80°C for longer periods. Any temperature above 60°C

will result in condensation accompanied by higher molecular weight and a reduction in reactive groups. These prior art resoles tend to have a final water content in the 10-20% range and are themselves intolerant to further process water. Their lower reactivity renders them incapable of rapid or full cure in the presence of excess water that is, by definition, a reaction by-product that will limit the degree of reaction. The only way to attempt to overcome this is to use extremely aggressive catalysts in the form of strong inorganic acids that are known to result in significant corrosion risk potential for any final product.

- 10 The technology of the present invention relies on the reactivity of the resole resin in conjunction with mild, often ester based, catalysts that result in final syntactic foam products that are essentially pH 'neutral' and safe in terms of corrosion risk.

The present required phenolic resole may be prepared, for example, from 116.5 parts of 44% formaldehyde solution to 100 parts of phenol flake in combination with 4.2 parts of 25% sodium hydroxide solution as a condensation catalyst. This reaction mixture is carefully raised to 60 (+/-2)°C with slow agitation and held there until a critical intermediate point is reached, as determined by viscosity measurement of the contents. This control viscosity should be 13.5-14.5sC at 25°C and is reached after 3-5.5 hours depending on scale. At this point, the contents are neutralized with *p*-toluene sulphonic acid to a pH of less than 7, preferably in the range 5.5-6.6. (A pH around 6 gives enhanced shelf-life compared to a pH between 7-8). Vacuum distillation is then carried out to a final water content of 3-4%, giving a resin with a viscosity of, preferably, 3,000-4,000cP at 25°C, further preferably having a free formaldehyde content of 3-5% and a free phenol content of 12-15%.

The resins may be mixed with one or more filling agents such as, but not limited to, water, boric acid, surfactants and chopped fibres (glass fibres, carbon and the like).

5 **Phenolic Resole Resin Catalysts:**

The acids that may be employed as catalysts include strong organic acids such as benzene sulphonic acid, toluene sulphonic acid, phenol sulphonic acid, xylene sulphonic acid, β -naphthalene sulphonic acid and α -naphthalene sulphonic acid.

10 Conventionally, strong inorganic acids may be used to cure phenolic resins but strong inorganic acids are not suitable for the purposes of the present invention. Preferred catalysts are esters of weak inorganic acids and include phosphate esters and blends of phosphoric acid with organic acids such as *p*-toluene sulphonic acid. Mixtures of any two or more of the acids and / or esters can also be used.

15

Suitable acidic catalysts are supplied by Borden Chemicals under the Trade Mark Phencat. Of the Phencat range, Phencat 10, 15, 381 and 382, either alone or in combination may be suitable for use in the present invention. Suitable phosphate ester-based catalysts are supplied by Chemische Fabrik Budenheim as Budit 380

20 and by Clariant AG as Hordaphos CCMS. Again, these may be used either alone or in combination with other acidic catalysts.

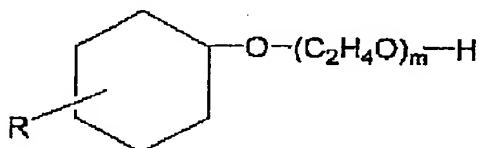
Although many acidic catalysts may be used for curing, each of the Examples -4 has it's preferred version. In a preferred embodiment (e.g., Example 4), the

25 catalysts may conveniently be blended with wet expanded thermoplastic microspheres to aid handling. This process itself is considered to be novel. The benefits are that volumes of two component systems may be made more equivalent and, secondly, that this approach allows the use of certain thermoplastic microsphere grades that are unstable (will dissolve) in the phenolic

30 resin.

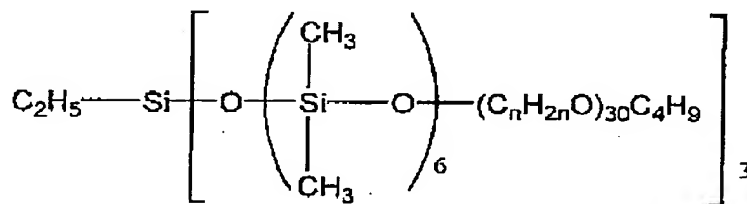
Surfactants:

In order to hasten mixing in the preparation of resole resin foams, a surfactant or surface active agent may be employed, beneficially a non-ionic surfactant such as the reaction or condensation product of an alkylene oxide having from 2 to 4 carbon atoms in the molecule with a compound such as higher alkylphenols having from 8 to 12 carbon atoms in the alkyl group, fatty acids having from 12 to 22 carbon atoms, and alkyl silanes and silicones. Among suitable surfactants are (a) the polyoxyethylene ethers of alkyl phenols having the general formula



wherein R is an alkyl group having from 8 to 12 carbon atoms and m is an integer from about 8 to 20, (b) ethoxylated castor oil and ethoxylated hydrogenated castor oil; i.e., the condensation product of said castor oils and from 8 to 20 mols of ethylene oxide per mol of said castor oil, (c) copolymers of ethylene oxide and propylene oxide containing from 8 to 20 moieties of each of said alkylene oxides, and alkyl silane polyoxyalkylene block copolymers similar to those described in US-A- 2,834,748.

Beneficially, the surfactant, or the mixture thereof, is the condensation product of ethylene oxide and nonyl phenol having a molecular weight of about 880, or an alkyl silane/alkylene oxide block copolymer of the formula



wherein $C_nH_{2n}O$ is a mixed oxyethylene/oxypropylene block of about 17 oxyethylene units and about 13 oxypropylene units.

- 5 Most preferred surfactants include those marketed by Dow Corning Corporation under the Trade Mark DC 193 and comprising an alkylsilane / alkylene oxide block copolymer.

Syntactic Phenolic Foam Composition:

10

Once heat is applied to a catalysed resin/microsphere blend, it is important that crosslinking of the resin occurs rapidly after full expansion in order to avoid cell rupture. In the case of the ready expanded material, speed is also required for the same reason although a protracted low temperature cure will also work. This is one of the primary reasons behind the choice of a highly reactive, polyfunctional phenolic resole resin. The advantage of this resin is that the reactivity may be readily modified by the inclusion of water or higher molecular weight ('slow') resole without affecting it's ability to fully cross-link and achieve maximum physical properties. This is not typical of conventional phenolic resoles.

15

20

Application of heat for curing may be via conduction (heated mould) or through the use of Microwave, Radio Frequency or Long Wave Infrared energy. The system's reactivity should be balanced to allow optimum material flow and expansion followed by rapid cross-linking. It is also possible to use exothermic heat to cure a mixture but this proves much more variable and harder to control.

25

Invariably, exothermic heat is involved anyway but it should not dominate. In order to achieve optimum syntactic foam properties, the matrix should be cross-linked in less than 15 minutes, preferably less than 10 minutes, more preferably less than 5 minutes.

30

Unexpanded microspheres may be added in the 0-40% (w/w), preferably 10-25% (w/w). Above 25% (w/w), extra material does not readily produce greater volume

since it appears to reach an efficiency peak. Wet expanded microspheres may be blended in a weight ratio of up to 5:1 of the wet microspheres to resin, preferably 10-20% (w/w) for the purposes illustrated in Example 3.

5 **Properties of the Syntactic Phenolic Foam Composition:**

The thermoplastic microspheres are themselves very flammable whilst cured phenolic resin is dense and brittle. Conventional phenolic foams are weak and friable for this reason.

10

The syntactic phenolic foams of this invention are semi-resilient and non-friable (comparable with other structural foams). Densities may be produced in the range 40 - 500kg/m³ depending on formulation and additives. Despite the apparently flammable microsphere content, these syntactic foams prove to be highly resistant
15 to temperature and fire, probably due to the solubilisation of the polymer shell of the microspheres by the phenolic resin. Desirable flame stability is also observed whereas conventional phenolic foams and resin are often subject to spalling/punking.

20 The fatigue resistance of these syntactic phenolic foams has also been shown to be equivalent to high performance structural foam cores (e.g., marine grade PVC foam).

The syntactic phenolic foams of this invention display desirable processing
25 flexibility depending on the ratio of resin to microspheres and whether expanded and/or unexpanded microspheres are used. At one end of the scale, the system is castable/pourable and may or may not expand. At the other end, the system is compression-mouldable dough.

30 **Example 1:**

"PyroFend" (Trade Mark) - a 10% (w/w) addition of unexpanded microspheres and 25% addition of water followed by 150-200%wt addition of boric acid. This results in a castable expanding syntactic phenolic foam of $\sim 400\text{kg/m}^3$ density that is highly fire quenching and thermally stable - suitable for extreme fire protection requirements.

A master-batch is produced from the following components:

	Phenolic resin J20/1235L (Borden Chemical)	100 parts
10	Expancel 551DU-40 (Casco Products)	10 parts
	Surfactant DC193 (Dow Corning)	1 part
	Water	25 parts

The above materials are readily blended with low shear mixing equipment. The master-batch may be stored for extended periods of 2-6 months depending on storage temperature (ideally 5-20°C). After storage, it should be re-mixed prior to use.

On a daily basis, granular boric acid (specifically Optibor TG from Borax Corp.) is added to an appropriate quantity of the master-batch at 150% w/w. This mixture is then kept agitated in a suitable mixing vessel that is capable of keeping all the materials efficiently mixed. The resinous master batch is preferably used at a temperature of 40-45°C for optimum control of moulding. Once heated to this temperature, the uncatalysed mixture is only stable for a period of ca. 30 minutes.

Heating may therefore be affected by the use of an in-line heat exchanger just prior to catalysation and dispensing or, alternatively, by pre-heating the boric acid to 80-85°C and adding this on a batch scale that may be dispensed within the above time limit.

Tooling for the manufacture of panels or three-dimensional structures is pre-heated to a temperature of 75-80°C. The mixture above is then catalysed with 10-

11% wt. (with respect to the master-batch) of an acidic catalyst such as Phencat 10 from Borden Chemical. This is preferably carried out by accurately dispensing the two liquid streams (of the resinous master batch and of the catalyst) into a static mixer and then directly into the mould. Catalysation of a large mass of material is risky unless it can be used within approx. 5 minutes. Moulds should be orientated so as to produce the maximum possible liquid depth at their base. 40% of the mould volume should be dispensed by weight, i.e. for every litre of mould volume, dispense 400g of the reactive system.

10 If the above procedure is correctly carried out, then moulds will be filled due to the expansion of the syntactic foam in 4-6 minutes. The syntactic foam is cured for handling purposes in 10-15 minutes from the start of dispensing.

15 The cured material with appropriate skins of either phenolic composite or steel is capable of giving high resistance to cellulosic and hydrocarbon pool or jet-fire conditions at low thickness. One hours insulation resistance is given by as little as 25mm thickness whilst greater than 2 hours resistance is possible from 50mm thickness. After fire exposure, the charred syntactic phenolic foam is still rigid and semi structural.

20 The material of the above example has also been tested successfully in advanced lightweight paper and data fire protection devices as well as in moulded covers for critical actuator devices in both the building and offshore industry.

25 **Example 2:**

'PyroPhen'(Trade Mark) - the basic invention of Example 1 with 25%wt. addition of unexpanded microspheres designed for the production of flat sheet or three-dimensional products. A key feature is the syntactic foam's ability to impregnate skins of fibrous reinforcement (e.g., glass, carbon, etc.) whilst expanding to produce an integral one-step sandwich panel. This can be carried out by forming

a pre-preg of the catalysed syntactic foam system between reinforcement layers or simply by pouring the system between dry reinforcement and allowing it to expand under the application of heat.

- 5 A master-batch is produced from the following components:

Phenolic resin J20/1235L (Borden Chemical)	100 parts
Expancel 551DU-40 (Casco Products)	25 parts
Surfactant DC193 (Dow Corning)	1 part

10

The above materials are readily blended with low shear mixing equipment. The master-batch may be stored for extended periods of 2-6 months depending on storage temperature (ideally 5-20°C). It should be re-mixed after storage and prior to use.

15

The above master-batch, known as PT774, is used with the addition of 0-15% (w/w) Expancel 551WE-40-d36 expanded microspheres in water and/or 0-15% (w/w) water. These additives must be added on a daily basis to avoid instability problems. The resultant mixture should ideally then be mixed or recycled in temperature-controlled environment to ensure that the mix achieves a stable temperature in the 20-25°C range.

20

Moulds or flat-sheet tooling must be held in a hydraulic press at 60-65°C. The mixture above should be catalysed with 10-15% (w/w) of a formulated acidic

25

catalyst (50% Phencat 15/50% Budit 380 ex Chemische Fabrik Budenheim (w:w)) just prior to dispensing, ideally through a static mixer, as in Example 1. The dispensing of 10-12% (w/w) of the catalysed system with respect to the volume of the mould will produce a tough, lightweight phenolic syntactic foam with a density of 100-130kg/m³ within 15-20 minutes, having a compressive strength of

30

0.7 – 1.0 MPa and a flexural strength >2 Mpa.

The use of microwave or radio frequency energy to expand and cure the syntactic phenolic foam is able to produce a foam with a density as low as 40kg/m^3 .

Syntactic phenolic foam of the above example offers a thermal conductivity (k or lambda value) of $0.030 - 0.035\text{ W/m/K}$ as well as good acoustic and impact properties. It is valuable as a core material in advanced lightweight, fire resistant structures, especially in aerospace and transportation where it complies with international standards for flammability, flame spread, smoke/toxic fume emission, heat release, etc. Ultimate performance is dependent on design and the material is readily suited to low weight fire barrier applications.

Example 3:

A matrix for insulative building panels based on polystyrene beads. Here the microsphere additive is around the 10% (w/w) level of either the unexpanded or wet expanded grade. The resulting panels are both stronger and more insulative than polystyrene foam alone whilst offering a significant level of fire resistance. On a daily or batch basis, the following blend is prepared in a suitable mixing vessel:

20

Phenolic resin J20/1235L (Borden Chemical)	100 parts
Expancel 551WE 40 d36 (Casco Products)	10 parts
Surfactant DC193 (Dow Corning)	2 parts
Boric acid (Optibor TG ex Borax)	20

25

A known weight of 35 kg/m^3 polystyrene beads with a particle size 2-6mm (e.g., ex Springvale) is transferred to a high volume device, such as a ploughshare mixer. The above resinous blend is then catalysed with 5% (w/w) Phencat 10 (Borden Chemical), ideally via a static mixer/dispenser as in above examples.

The catalysed system is added to the beads with agitation in a mass ratio of 1.2:1

30

(Resin/catalyst mix: polystyrene beads) and mixing is maintained for 1-2 minutes so that the beads are evenly coated.

Compression moulds are prepared with the ability to give 40% over-pack volume.

- 5 The coated beads are then transferred to the moulds and levelled at the 140% mark. The moulds are then compressed in a suitable device such as a hydraulic press down to their 100% mark with heating in the range 60-80°C. Handleable panels are produced within 10-15 minutes in this way. Use of microwave or radio frequency energy can significantly reduce this cure time to around 2 minutes.

10

The syntactic, boric acid containing matrix that encapsulates the polystyrene beads produces a stronger and more thermally insulating structure than straight polystyrene foam, whilst producing a stable carbon skeleton in a fire resistance scenario. Approximately 45 minutes insulation resistance against a cellulosic fire curve (e.g., BS476 Pt22/ ISO 834) is achievable from a 100mm panel of this example with 1mm steel skins. The requirement is typically 30 minutes.

15

The table below gives strength and fire resistance data results:

Property	Units	Value	Method of test
Density	gms/litre	47	
Lambda	mW/m ² K	34	
Acidity	pH	7.84	
Max Flame Spread parameter FSP _c	s ^{-1/2}	0.37	ANSI/FM 4880 April 2001
5 sec average FSP _c	s ^{-1/2}	0.33	
Thermal Response Parameter TRP	kWs ^{1/2} /m ²	166	
Critical Heat Flux for Ignition CHF	kW/m ²	20	
Maximum Heat Release Rate	kW/m ²	144	
Heat of Combustion	KJ/g	30	

20

The density figure given above compares very favourably with Lamella Rockwool at 124 gm/l, but it is only approximately twice the density of conventional Expanded Polystyrene (EPS) insulation board.

- 5 The Lambda figure at 34mW/m²K is marginally better than that quoted for conventional high density EPS, but it is much better than Lamella Rockwool, quoted at 42mW/m²K.

- 10 The acidity figure is significant in that the vast majority of products containing phenolic resin have acidic properties, with pH levels between 2 – 4. This product with pH at 7.84 is expected to have none of the corrosive tendencies normally associated with phenolic foams.

- 15 All the fire related figures are summarised through calculation of the '5 second average FSP_c'. The value obtained for the product of 0.33 is well within the range allowed (less than 0.52) under the stated standard as a core acceptable for panels used in external envelopes and other sections of the Factory Mutual approved building.

- 20 Of course, the above approach would also be effective with other lightweight materials having a particle size of greater than 2mm, a specific gravity of less than 1.0 and a low volumetric cost, e.g., recycled foam, cork, etc.

Example 4:

25

Compression mouldable, dough-like materials with a wet expanded microsphere ratio of 2:1 - 4:1 on resin. Densities of between 60 - 150 kg/m³ are achievable.

1kg Expancel 551WB is blended with a pre-mixture of:

- 30 20g Phencat 15
 20g Phencat 382

17

2g Gold Cup Red (water based pigment dispersion)

in a planetary mixer until the colour is evenly distributed. To this syntactic catalyst, a phenolic resin blend of:

- 5 200g J20/1235L phenolic resin (Borden Chemical)
- 2g DC193 surfactant (Dow Corning)
- 2g Gold Cup Blue (water based pigment dispersion)

- is added along with 20g 13mm glass fibres. The whole is blended to an even
- 10 colour change and then charged to a mould pre-heated to 65°C.

- The catalysed material is compressed by at least 25% during which time ca. 40% wt. water is released from the mould. After 2 hours curing in the mould, the syntactic foam panel is released and dried/post-cured in a recirculating oven at
- 15 80°C. In this example, the longer curing time is caused by the quantity of water in the system, i.e. >50 – 70% (w/w).

- When all water has been removed, this ultra lightweight, resilient phenolic syntactic foam has a density of ~40kg/m³ and a lambda value of less than 0.03
- 20 W/m/K.

The present invention is not limited to the embodiments described herein, which can be amended or modified without departing from the scope of the present invention.

